

Mn and Ce XAS Studies of $\text{Ca}_{2-x}\text{Ce}_x\text{Mn}_3\text{O}_7$

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 Beamline(s): X19A, X18B

Perovskite based transition metal (T) compounds, like the layered Ruddlesden-Popper $(\text{AO})(\text{ATO}_3)_n$ compound series, have been the subject of intense research due to their fascinating/useful magnetic and transport properties. We have been studying the $n = 2$ compound $\text{Ca}_{3-x}\text{Ce}_x\text{Mn}_2\text{O}_7$ for several reasons. The lower dimensionality of the perovskite layers is known to influence the magnetic/structural transitions in such materials. The electron-doping regime is less explored in manganite compounds. The potential of two electron donation per dopant also offers an intriguing and almost unexplored area in this field. The first question to be addressed is the Ce^{3+} vs Ce^{4+} character of the dopant. In Figure 1 we compare the Ce-L₃ edge of an $x = 0.15$ sample in this system to Ce standard compounds. The strongly bimodal character and chemical shift of the $x = 0.15$ spectrum (and all x 's studied) clearly defines a formally Ce^{4+} character in the $\text{Ca}_{3-x}\text{Ce}_x\text{Mn}_2\text{O}_7$ system. Interestingly the sharp bimodal B-A features in this system stands in contrast to the more complicated sub-splittings observed in CeO_2 and could potentially be of interest in the field of mixed valent Ce compounds.

The Mn-K edge measurements on a series of $\text{Ca}_{3-x}\text{Ce}_x\text{Mn}_2\text{O}_7$ compounds, along with standards, are shown in Figure 2. The continuous shift of the Mn-main edge to lower energy with Ce substitution clearly evidences the controlled Mn^{3+} to Mn^{4+} conversion upon the electron doping. Selected Mn pre-edge spectra (inset of Figure 2) confirm the Ce electron doping. Detailed comparison to other systems verify the rate of doping as 2 electron per Ce substituted

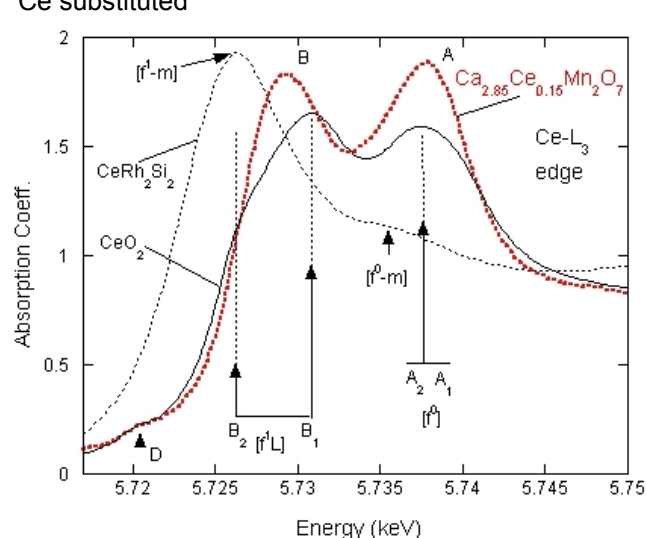


Figure 1. The Ce-L₃ edges of: $\text{Ca}_{3-x}\text{Ce}_x\text{Mn}_2\text{O}_7$ ($x=0.15$); the fluorite structure compound CeO_2 ; and, for comparison, the "nearly- Ce^{3+} ", metallic (m) compound CeRh_2Si_2 . The f^0 and f^1L labels refer to the Ce^{4+} - $4f^0$ and Ce^{3+} - $4f^1$ related final state features. The perovskite based compound spectrum is characteristic of a formally Ce^{4+} compound.

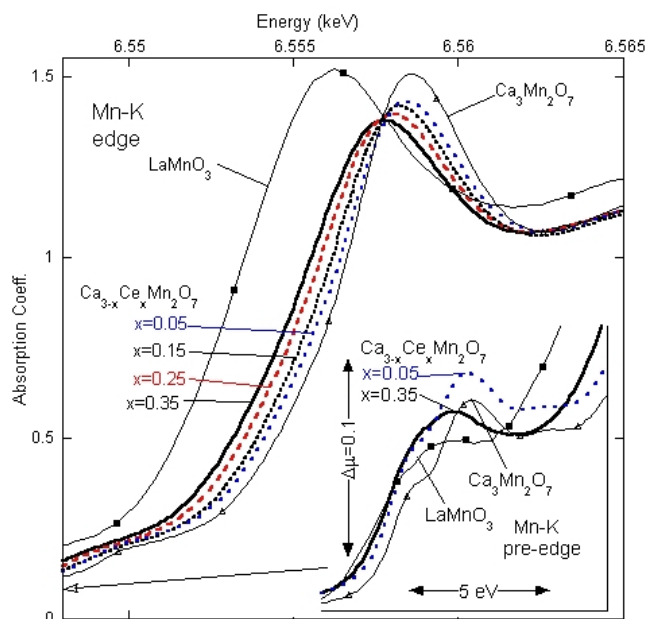


Figure 2. A comparison of the Mn-K edges of Mn^{3+} - LaMnO_3 , Mn^{4+} - $\text{Ca}_3\text{Mn}_2\text{O}_7$, and a series of $\text{Ca}_{3-x}\text{Ce}_x\text{Mn}_2\text{O}_7$ compounds. Note the chemical shift of the Mn-main edge indicating the Ce induced electron doping. The inset illustrates the pre-edge feature evolution with greater Mn^{3+} -character being introduced by the Ce substitution.